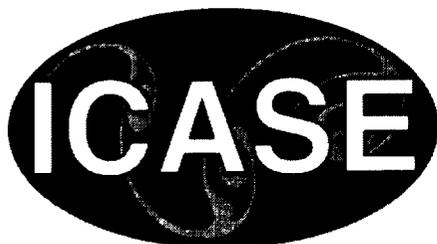


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In Situ Poling and Imidization of Amorphous Piezoelectric Polyimides

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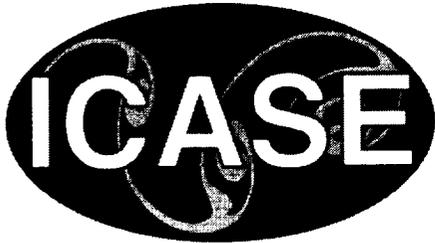
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IN SITU POLING AND IMIDIZATION OF AMORPHOUS PIEZOELECTRIC POLYIMIDES

CHEOL PARK¹, ZOUBEIDA OUNAIES¹, KRISTOPHER E. WISE¹, AND JOYCELYN S. HARRISON²

Abstract. An amorphous piezoelectric polyimide containing polar functional groups has been developed using a combination of experimental and molecular modeling for potential use in high temperature applications. This amorphous polyimide, (β -CN)APB/ODPA, has exhibited good thermal stability and piezoelectric response at temperatures up to 150°C. Density functional calculations predicted that a partially cured amic acid (open imide ring) possesses a dipole moment four times larger than the fully imidized closed ring. *In situ* poling and imidization of the partially cured (β -CN)APB/ODPA was studied in an attempt to maximize the degree of dipolar orientation and the resultant piezoelectric response. A positive corona poling was used to minimize localized arcing during poling and to allow use of higher poling fields without dielectric breakdown. The dielectric relaxation strength, remanent polarization, and piezoelectric response were evaluated as a function of the poling profile. The partially cured, corona poled polymers exhibited higher dielectric relaxation strength ($\Delta\epsilon$), remanent polarization (P_r) and piezoelectric strain coefficient (d_{33}) than the fully cured, conventionally poled ones.

Keywords. *in situ* poling, amorphous polyimide, piezoelectricity, polarization, modeling

Subject classification. Structure and Materials

1. Introduction. Polymers containing dipolar functionalities have been studied as piezoelectric materials for many applications since the discovery of poly(vinylidene fluoride) (PVDF) [1], currently the only commercially available piezoelectric polymer. Majority of piezoelectric polymers are semicrystalline and usually need a favorable morphology to be efficiently polarized under an electric field, which often requires extensive mechanical stretching to attain a desirable conformation prior to poling. After poling, the aligned dipoles in these semicrystalline polymers are prone to mechanical relaxation at temperatures well below their Curie temperatures. Some amorphous polymers containing strong dipoles have also received great attention for their piezoelectric response because they usually do not require special treatment prior to polarization of the dipoles [2-7]. These amorphous piezoelectric polymers, however, usually exhibit much lower piezoelectric response than semicrystalline polymers. One exception, a vinylidene cyanide and vinyl acetate copolymer has been extensively studied because its piezoelectric response is comparable to PVDF [3-7]. A cooperative motion of four monomer units in a locally ordered structure has been proposed to explain the high dielectric relaxation strength [5]. Although an unusually high dielectric relaxation strength ($\Delta\epsilon/\epsilon_0 \approx 125$) was observed in this copolymer, this value was achieved only after drawing prior to poling. More extensive study has been hampered by difficulty in synthesis of the copolymer.

Recently, a series of amorphous piezoelectric polyimides containing polar functional groups have been developed at NASA Langley, based on molecular design and computational chemistry, for potential use in high temperature applications [8-10]. One of these, a polyimide containing a single cyano group, (β -CN)APB/ODPA, retains more than 50% of its room temperature remanent polarization at 150°C for 500 hours¹¹. The piezoelectric response of this polyimide is, however, an order of magnitude smaller than

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that of PVDF. This is in part arisen from the fact that the dipoles in the polymer do not align along the applied electric field efficiently because of limited chain mobility in the imidized closed ring structure. To increase the piezoelectric response of these polymers, two different approaches have been studied. The first approach uses “structural control” to increase the dipole concentration of the monomer unit by designing a new polymer [10]. The second approach uses “process control” to maximize the dipole orientation in a given structure by adjusting the poling process [11].

In the present study, the process control approach was employed to maximize the piezoelectric properties of the (β -CN)APB/ODPA. Prediction of piezoelectric behavior in amorphous polymer systems is complicated by interplay of electronic and conformational effects [12]. We describe some recent results of an ongoing study aimed at better understanding this behavior using molecular modeling. These results indicate that a partially cured amic acid (open imide ring) exhibits higher net dipole moment than the fully imidized closed ring. *In situ* poling and imidization processing of a partially cured (β -CN)APB/ODPA was employed to achieve efficient dipolar orientation. Positive corona poling was used to minimize localized arcing during poling and to enable use of a higher poling field without dielectric breakdown. The dielectric behavior, remanent polarization, and piezoelectric responses were assessed as a function of frequency and temperature.

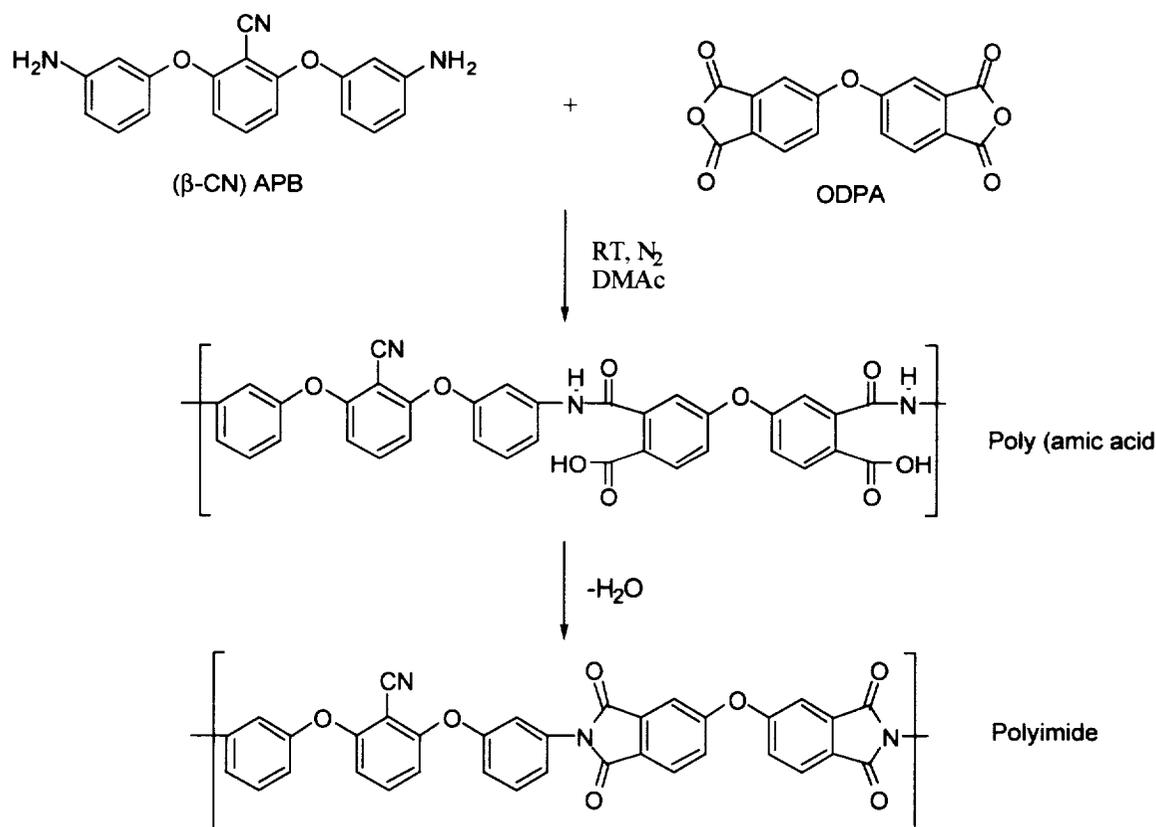


FIGURE 1. Scheme of (β -CN)APB/ODPA polymerization.

2. Experimental.

2.1. Materials. The polyimide studied, (β -CN)APB/ODPA, was prepared from 2,6-bis(3-aminophenoxy) benzonitrile ((β -CN)APB) and 4,4' oxidiphthalic anhydride (ODPA) via a poly(amic acid) solution in N,N-dimethylacetamide. The scheme is shown in Figure 1. Details of the synthesis of (β -CN)APB/ODPA have been described elsewhere [9]. The poly(amic acid) solution was cast onto a clean, dry glass plate using a doctor's blade in a low-humidity air chamber. The cast films were then dried in the chamber at room temperature overnight to form tack-free films. The dried films, approximately 30 μm films in thickness, were cured under various cure cycles in an oven purged with nitrogen at a heating rate of 2°C/min to produce samples with different degrees of imidization. The various cure cycles are summarized in Table 1. A silver layer, approximately 200 nm thick, was evaporated on both sides of the films for conventional poling and on only one side of the films for corona poling.

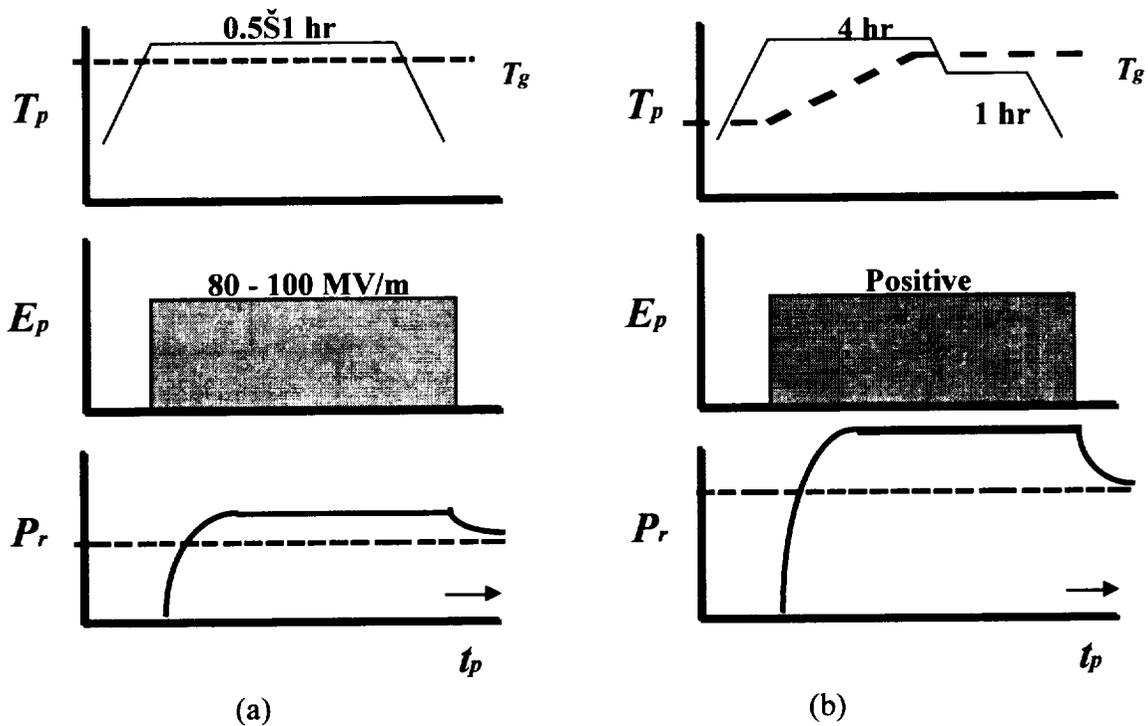


FIGURE 2. Poling profiles: (a) conventionally poled and fully cured, (b) corona poled and partially cured polyimide.

2.2. Poling procedure. Film specimens were poled using either a conventional or a positive corona poling procedure. For the conventional poling, each sample was polarized by application of a DC electric field ($E_p = 80 \text{ MV/m}$) at an elevated temperature ($T_p = T_g + 5^\circ\text{C}$) in a silicone oil bath for a selected poling time (t_p). For corona poling, a DC voltage of 20 kV was applied to generate a positive corona at the tip of a single tungsten wire for four hours at 223°C and one hour at 212°C using a mica hot plate. The distance between the corona tip and the specimen was 30 mm. The corona poling setup was enclosed in a Plexiglass box, which was purged with argon gas during the poling process. For both poling processes, the dipoles were oriented with the applied field at a poling temperature (T_p) above T_g , with subsequent cooling to below T_g in the presence of the applied field. The poling profiles of the conventional and corona poling are shown in Figure 2 and the corona poling set-up is illustrated in Figure 3. The resultant remanent polarization (P_r) is estimated from the following equation [13],

(1)

$$P_r = \epsilon_0 \Delta\epsilon E_p$$

where ϵ_0 is the permittivity of free space (8.854 pF/m), $\Delta\epsilon$ is the dielectric relaxation strength, and E_p is the poling field. The dielectric relaxation strength ($\Delta\epsilon$) is defined as the change in dielectric constant when a polymer transforms between unrelaxed (below T_g) and relaxed (above T_g) states. The piezoelectric response is directly proportional to the remanent polarization (P_r).

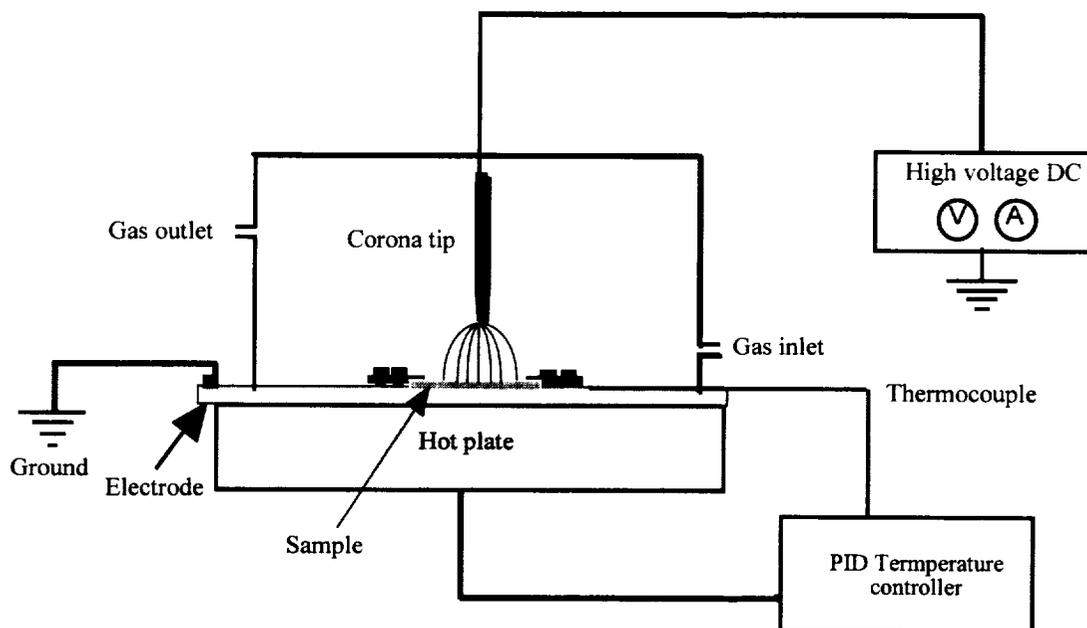


FIGURE 3. Schematic of corona poling set up.

2.3. Characterization.

2.3.1. Degree of imidization. The glass transition temperatures (T_g) of the films were measured by differential scanning calorimetry with a Shimadzu DSC-50 at a heating rate of $10^\circ\text{C}/\text{min}$ in air. The T_g was taken as the inflection point of the shift of the baseline of the DSC thermogram. The degree of imidization was determined by a Nicolet FTIR spectrometer in an ATR mode with a Nicolet Continuum IR microscope. The absorption peak at 1780cm^{-1} (symmetric carbonyl stretch) was used to determine the degree of imidization and that at 1380cm^{-1} (ring breathing modes of the aromatic moieties) was used as an internal standard [14]. The results are presented in Table 1.

TABLE 1
Processing parameters and properties of partially-cured, corona poled (β -CN)APB/ODPA.

Sample	Cure cycle ($^\circ\text{C}$) 1 hour each, N_2	T_g before poling ($^\circ\text{C}$), DSC	$A_{1780\text{cm}^{-1}}/A_{1380\text{cm}^{-1}}$ FTIR	P_r (mC/m^2)
P100	50, 100	97	0.18	N/A
P150	50, 150	142	0.69	38
P200	50, 150, 200	166	0.82	10
P240	50, 150, 200, 240	218	1.00	14*

* P_r was measured from conventionally poled P240.

2.3.2. Dielectric measurement. The dielectric constant and loss of unpoled polyimide samples were evaluated as a function of temperature and frequency in a SUN System environmental oven with a Hewlett Packard 4192A Impedance Analyzer. The measurements were performed from room temperature to 300°C at a heating rate of 1°C/min at 5, 10, 100 and 1k Hz. These measurements yield the dielectric relaxation strength $\Delta\epsilon$, which is a parameter of greatest interest in designing amorphous polymers with large piezoelectric activity [13].

2.3.3. Thermally stimulated current (TSC) measurement. After poling, the remanent polarization (P_r) was measured as a function of temperature. As the sample was heated through its T_g at a heating rate of 1.0°C/min, the depolarization current was measured using a Keithley 6517 electrometer. The remanent polarization (P_r), equal to the charge per unit area, was obtained from the data by integrating the current with respect to time and plotting it as a function of temperature. This is given by,

$$(2) \quad P_r = \frac{q}{A} = \frac{1}{A} \int i(t) dt$$

where q is the charge, A is the electrode area, i is the current, and t is the time.

2.3.4. Piezoelectric strain coefficient measurement. Displacement measurements were performed using a non-contacting fiber optic sensor manufactured by Opto-Acoustic Sensors. Sinusoidal waveforms at a frequency of 1 Hz were used for all measurements. Multiple samples were measured at each condition, and the average displacement was recorded. Out-of-plane polymer motion is determined by monitoring the intensity of the light reflected from the polymer surface. As the surface of the piezoelectric films moves away from the sensor tip, the signal decreases, and as the surface moves closer to the sensor tip, the signal increases. The out-of-plane strain (S_{33}) was measured in response to the applied electric field (E), which is given by,

$$(3) \quad S_{33} = \Delta t / t$$

where, t is the thickness of the polymer, and Δt is the change in thickness. The piezoelectric strain coefficient, d_{33} , was obtained based on the following equation assuming a zero-stress boundary condition.

$$(4) \quad S_{33} = d_{33} \cdot E$$

3. Results and Discussions

3.1. Computational chemistry. In this section, we indirectly address the poling behavior and piezoelectric properties of (β -CN)APB/ODPA using a combination of molecular modeling techniques. We conceptually decompose the polarization response of a polymer into electronic, conformational, and orientational components. Electronic polarization refers to the transient reorganization of the electron density about an essentially fixed nuclear configuration. Conformational polarization describes the rotational response of small fragments or functional groups of the polymer that results from the coupling of 'local dipoles' to the external field. A local dipole is not a rigorously defined property of a molecule, but it is a useful mental model for visualizing the response of relatively rigid and electronically distinct fragments to an external field. We have chosen to use the term conformational polarization for this type of response to distinguish it from the more commonly used classifications of atomic polarization, which refers to small changes in bond distances or angles, and orientational polarization. Finally, orientational polarization describes the larger scale motions of segments of the polymer backbone. Obviously, this decomposition of the polarization response is artificial: electronic polarization is tightly coupled with

conformational polarization, which is, in turn, tightly coupled with orientational polarization. Making this conceptual division is necessary, however, to bring studies of this kind within range of existing theoretical and simulation capabilities. The results presented in this section are restricted to conformational polarization, thus neglecting the electronic and orientational components for the time being.

As described in other parts of this paper, we are primarily interested in the relative response to poling and retention of polarization between the partially and fully cured forms of $(\beta\text{-CN})\text{APB}/\text{ODPA}$. Inspection of Figure 4 reveals that the primary difference between the amic acid and the imide forms lies in the $(\beta\text{-CN})\text{APB} - \text{ODPA}$ linkage region. The difference in conformational polarizability of the partially and fully cured forms must arise from the mobility in this region of the polymer (mostly from ODPA forms as that of $(\beta\text{-CN})\text{APB}$ is negligible). Another conceptual simplification is achieved by separating the mobility into a dipole - field response term, which acts to orient the monomers in the direction of the field, and a dihedral energy barrier that tends to hold the monomers (and the intermonomer linkage) in its minimum energy configuration, which is generally not aligned with the field. In what follows, we examine some limiting cases to better understand the overall phenomenon.

Considering the ODPA monomer of the uncured polymer, it is evident that there are several fragments, each with a local dipole, which may respond relatively independently of the others to the external field. The orientation of the individual fragments will, in turn, collectively increase the total dipole moment of the ODPA monomer. This process will lead to improved monomer scale conformational polarizability, and even improved orientational polarizability. In contrast, the fully cured imide form of the polymer has no independently polarizable fragments. Therefore, any monomer level conformational

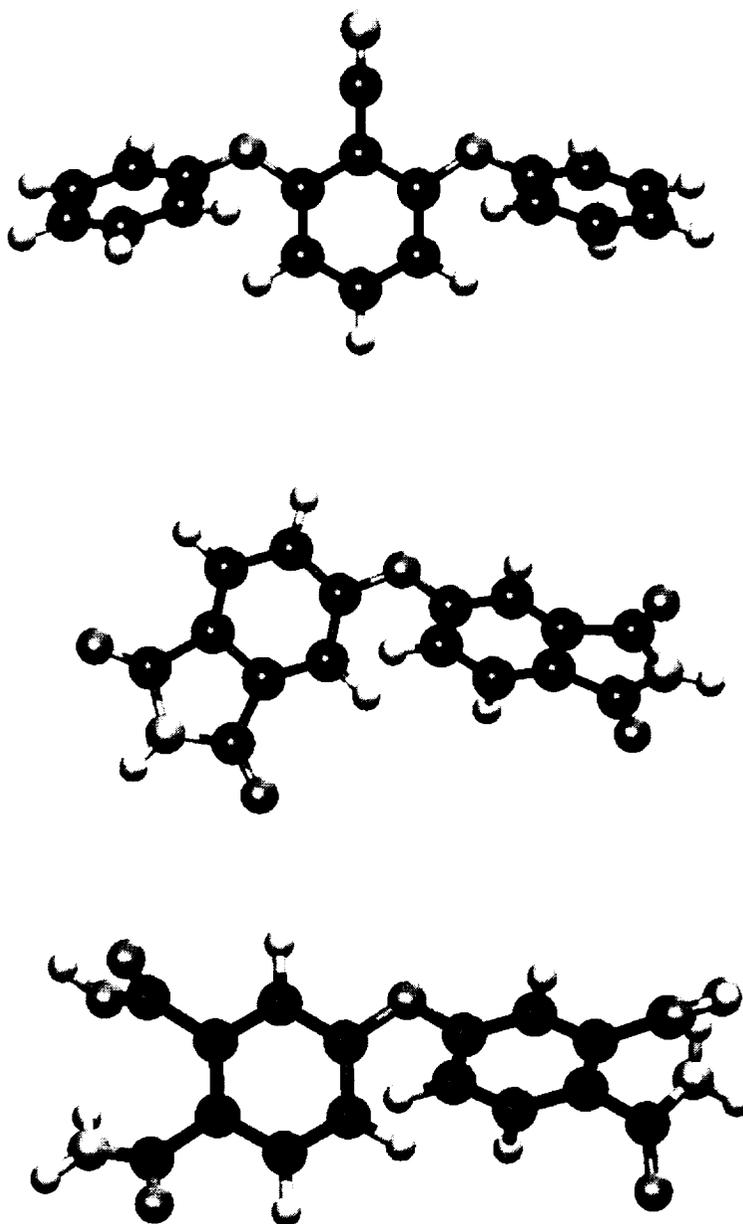


FIGURE 4. Molecular structures of monomers illustrating their conformations; (a) $(\beta\text{-CN})\text{APB}$, (b) cured, oriented ODPA (1.9D), (c) uncured, oriented ODPA (8.8D).

polarization or higher order orientational polarization must result from the intrinsic dipole of the rigid monomer.

To test the validity of this qualitative argument, we have carried out a series of calculations on the three limiting forms of the ODPA monomer: the uncured monomer in its field-free configuration, the uncured monomer after orienting the functional groups in an external field, and the cured, imide form of the monomer. Field effects on the imide form are ignored as they have no influence on its conformation polarizability. In the cases of the field-free uncured monomer and the cured monomer, geometry optimizations [15] were performed using the B3LYP density functional method [16] with a 6-31G* basis set [17]. Conformational poling of the uncured monomer was simulated by performing a molecular mechanics [18] minimization of the structure subject to a static external electric field of the same magnitude as used in the experiments (80 MV/m). Atomic charges [19] were derived from the quantum chemical calculation mentioned above for the field-free, uncured monomer. The use of charges from a field-free calculation neglects any internal electronic polarization effects, as mentioned above. Angular and dihedral force constants were taken from the literature [20], and all internal bond distances were held fixed [21]. After minimizing the geometry in this way, a single point B3LYP/6-31G* density functional calculation was performed on the structure to calculate the dipole moment. The dipole moments calculated using this procedure are summarized in Table 2.

TABLE 2
Dipole moments calculated of the cured and uncured, unoriented and uncured, oriented ODPA monomers.

ODPA – Cured	ODPA – Uncured, Unoriented	ODPA – Uncured, Oriented
1.9D	4.6D	8.8D

The results in Table 2 clearly support the arguments made above. The uncured, field oriented monomer has a dipole moment almost twice as large as the uncured, unoriented monomer. Likewise, the uncured, unoriented monomer has a dipole moment more than double that of the cured, imide form of the polymer (either unoriented or field oriented). Comparing the uncured oriented monomer with the cured monomer reveals a factor of four difference in dipole moment. Since a statistical majority of the uncured ODPA monomers in the poling experiment will tend to be in an oriented conformation, the uncured amic acid form of the polymer will obviously be much more polarizable than the fully cured polyimide. This conclusion is in agreement with the experimental work reported in this paper.

3.2. Degree of imidization. A fully cured (β -CN)APB/ODPA sample was prepared from the dried tack-free polyamic acid film by thermal cure at 50, 150, 200, and 240°C for an hour each under nitrogen atmosphere, which is denoted P240. Under this cure cycle, imidization of the amic acid appeared complete, and the glass transition temperature (T_g) was 218°C. For partially cured samples, the dried poly(amic acid) films were thermally imidized under nitrogen atmosphere at various cure cycles. The final cure temperatures of these samples were 100, 150, and 200°C, which are denoted as P100, P150, and P200, respectively. For the partially cured samples, the degree of imidization was estimated by measuring T_g and assessing FTIR spectra. The glass transition temperatures of the P100, P150, and P200 were 97, 142, and 179°C, respectively. The ratio of the FTIR absorption peak at 1780 cm^{-1} (symmetric carbonyl stretch) versus that at 1380 cm^{-1} (ring breathing modes of the aromatic moieties) was also used to estimate the degree of imidization, assuming the ratio is 1.0 for the fully cured P240 [14]. The ratio increased with the final cure temperature as seen in Table 1. For example, the partially cured P150 shows that T_g was 142°C and the ratio of A1780 cm^{-1} /A1380 cm^{-1} was 0.69, which implies that significant amount of the amic acid remained unimidized after 150°C final cure. Therefore, higher mobility of the dipoles is

expected for the polymers prepared at the lower final cure temperature. Table 1 summarizes the cure cycles, T_g s, and the FTIR absorption ratios.

The partially cured films were additionally imidized *in situ* during corona poling. To determine the poling profile, the imidization under the corona poling was monitored by measuring the T_g as a function of the cure time on the mica hot plate. Imidization appeared to be complete within one and a half hours at 223°C on the hot plate. Therefore, the corona was applied on the partially cured film for at least two hours at 223°C ($T_g + 5^\circ\text{C}$) to achieve complete imidization.

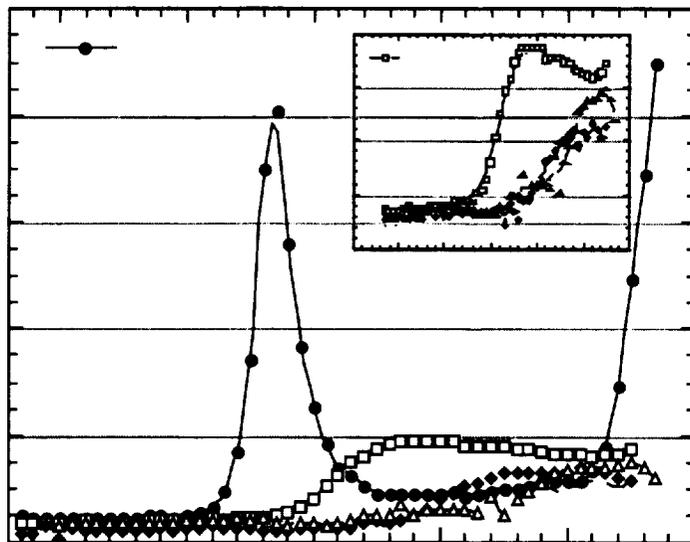


FIGURE 5. Dielectric behaviors of the films, P100, P150, P200, and P240, at 10Hz as a function of temperature.

3.3. Dielectric behavior. Computational modeling demonstrated that the uncured amic acid form of the polymer is much more polarizable than the fully cured polyimide. This higher polarizability can provide higher piezoelectric response. The piezoelectric response of a material can be predicted by the remanent polarization (P_r), which in turn can be estimated from the dielectric relaxation strength ($\Delta\epsilon$) according to Equation (1). The dielectric behavior of the polyimide films prepared at various cure cycles, P100, P150, P200, and P240, was studied as a function of temperature at various frequencies (0.01, 0.1, 1, and 10kHz). The dielectric responses of the films, P100, P150, P200, and P240, at 10Hz as a function of temperature are seen in Figure 5. A predominant peak appeared in the dielectric spectrum of P100 at around 110–160°C. This peak is likely due to the release of remanent water gained from the solvent DMAc and/or generated from condensation reaction by imidization of the amic acid during heating. This large amount of water evaporation often caused excessive premature local dielectric breakdown during the *in situ* corona poling, and thus P100 was excluded from the poling study. For the specimens cured at temperatures higher than 100°C, a noticeable dielectric relaxation appeared near T_g for each spectrum. In addition, the onset temperature of the relaxation increased with the final cure temperature. The dielectric relaxation strength ($\Delta\epsilon$) increased with decreasing final cure temperature, as shown in the inset of Figure 5. This occurs mainly because the dipoles in the polymer chain cured at the lower temperature have higher mobility due to the more flexible amic acid ODPA (open ring). The lower T_g value and the higher

amount of the unimidized amic acids in the FTIR spectra suggested the higher mobility of the polymer chain cured at the lower temperature. In addition, the total dipole moment of the optimized amic acid exhibits a higher dipole moment (4.6 Debye) than the cured imide ring (1.9 Debye) in the ODPA backbone, as shown by the *ab initio* computation. This might contribute to the increase of the $\Delta\epsilon$ as well.

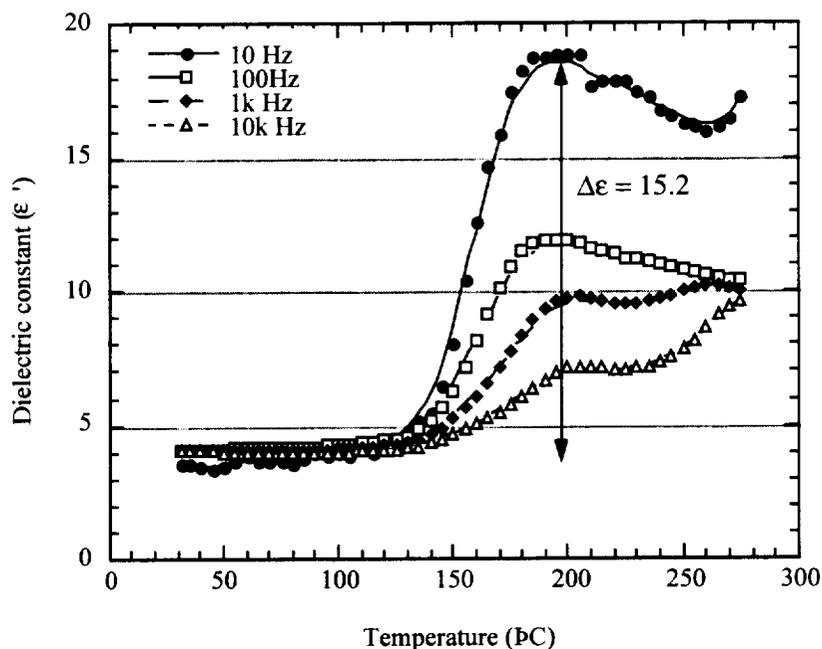


FIGURE 6. Frequency dependence of dielectric behavior for P150 as a function of temperature.

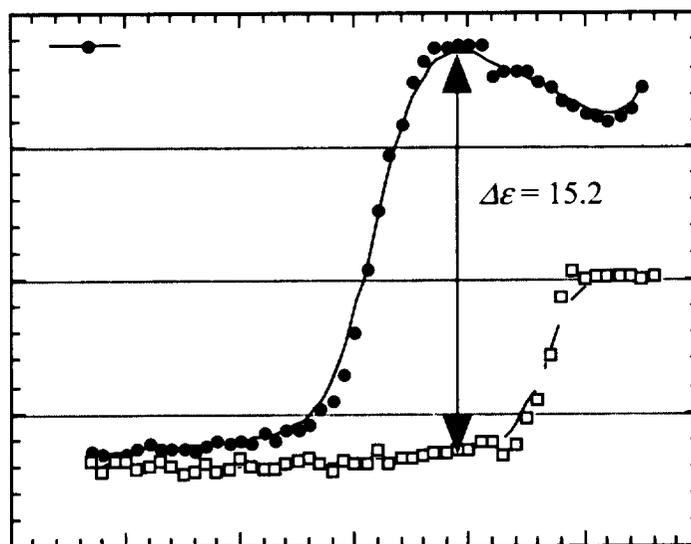


FIGURE 7. Dielectric constant of P150: first and second runs at 10 Hz.

Figure 6 shows the frequency dependence of the dielectric constant for P150 as a function of temperature. The dielectric relaxation strength ($\Delta\epsilon$) decreased with increasing frequency, while the onset temperature for the relaxation remained independent of frequency. This frequency sensitive dielectric behavior implies that $\Delta\epsilon$ originated mostly from the orientational (and conformational) polarization caused by the highly polar components such as the nitrile group. $\Delta\epsilon$ increased with decreasing frequency and reached a maximum of about 15.2 at 10Hz. It is expected that $\Delta\epsilon$ will be even higher as the frequency approaches zero (DC), where the corona was applied for the actual poling procedure. The value of $\Delta\epsilon$ at 1Hz was estimated by extrapolating the values of the $\Delta\epsilon$ as a function of frequency using a power law curve fit with a correlation coefficient of 0.97. Based on the curve fit, the value of $\Delta\epsilon$ at 1Hz for the partially cured P150 was 22.4 and that of the fully cured P240 was 15.1.

The second dielectric measurement of the partially cured P150 following the first run up to 280°C demonstrated a decrease in the $\Delta\epsilon$ and higher onset temperature as shown in Figure 7. A similar result was observed for the second dielectric sweep of the fully cured P240. The magnitude of the $\Delta\epsilon$ of the first run at 10Hz was 15.2 and that of the second run was about 7.0 for P150. These observations imply that the imidization is completed during the first dielectric sweep and the sample behaves like a fully cured sample in the second run.

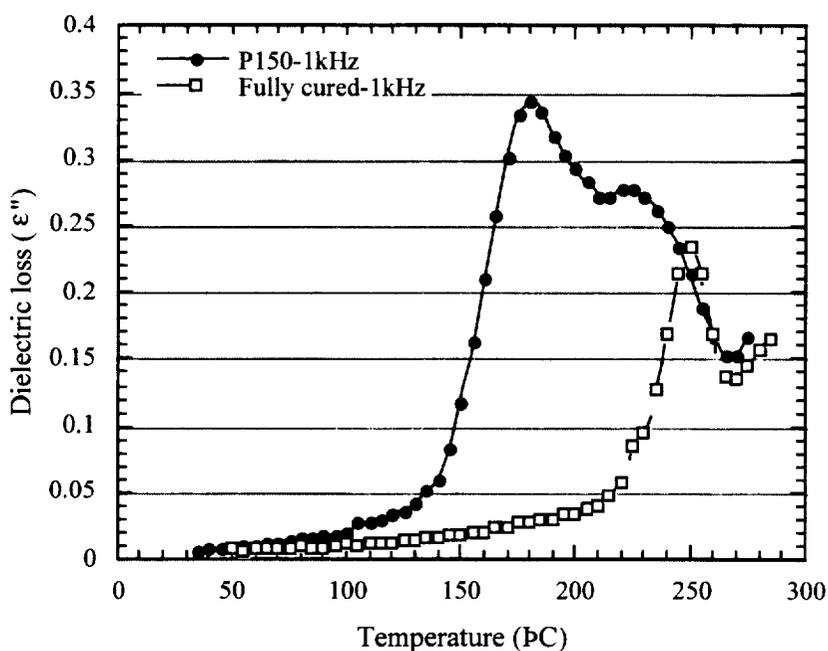


FIGURE 8. Dielectric loss of the partially (P150) and fully cured (P240) polyimides was also examined at 1kHz.

The dielectric loss of the partially cured (P150) and fully cured (P240) polyimides at 1k Hz is shown in Figure 8. The dielectric loss spectrum of the P150 was more dissipative than that of the P240, which is probably associated with the higher mobility of the partially imidized polymer molecules of the P150 and the presence of remanent solvent. Moreover, P150 exhibited double relaxation peaks while P240 showed a single peak at a higher temperature. The two relaxation peaks of the partially cured P150 spectra probably resulted from the coexistence of both the open amic acid (lower peak) and imidized closed ring structure (higher peak).

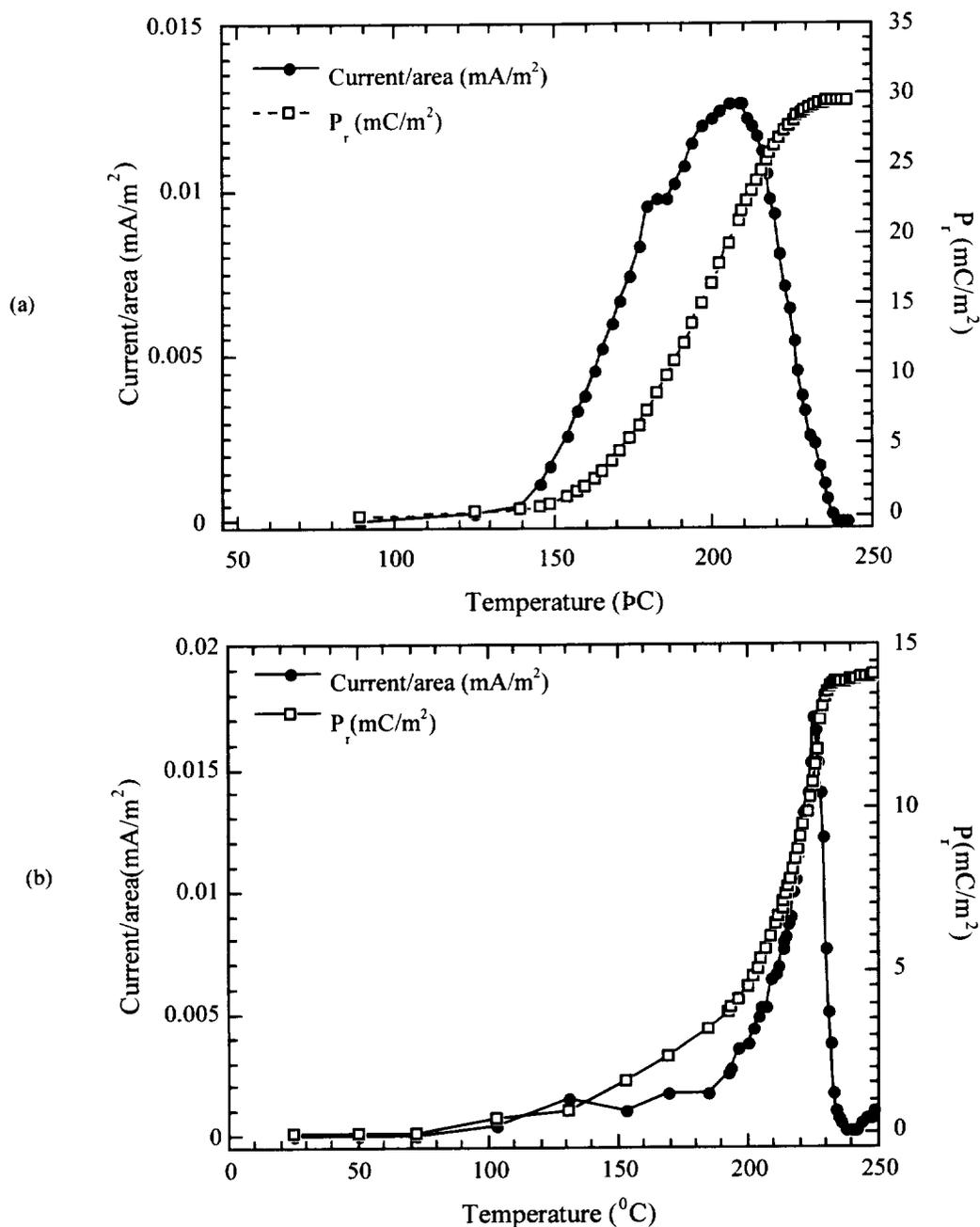


FIGURE 9. Typical TSC curves for conventionally poled P240 and corona poled P150 as a function of temperature.

The dipoles of the amic acids could align more efficiently at lower temperature in the presence of the corona field and some of these aligned dipoles will randomize as the temperature rises toward the final cure temperature due to thermal energy (Brownian motion) and progression of the imidization reaction. Nevertheless, some of the dipoles aligned close to the direction of the field may remain aligned to a certain extent along the corona field during the *in situ* poling and imidization procedure. Computational chemistry (section 3.2.) indicates that the total dipole moment of the uncured oriented amic acid form was approximately four times higher than that of the cured oriented one as seen in Table

2. Consequently, these metastably aligned dipoles before imidization should increase the overall remanent polarization.

3.4. Thermally stimulated depolarization current (TSC). The amorphous polyimides were poled above the T_g in a relaxed state to promote dipolar orientation, and then cooled slowly to room temperature while the applied electric field was being held to freeze the aligned dipoles. The degree of the alignment can be estimated by measuring the current released during heating of the polarized samples, which is called thermally stimulated depolarization current (TSC). Thermally stimulated depolarization current was measured for partially cured, corona poled polyimides and fully cured, conventionally poled polyimides. Figure 9 shows two typical TSC curves for conventionally poled P240 and corona poled P150 as a function of temperature. Depolarization of the conventionally poled P240 did not begin until the temperature reached about 20°C below T_g . At this temperature the depolarization current increased and then decreased rapidly, generating a sharp peak. In contrast, depolarization of the corona poled P150 began at a lower temperature (around 140°C), and a broader peak was obtained. The depolarization onset temperature of the partially cured samples appeared to be correlated with the T_g (142°C for P150) of the sample. The onset temperatures of P150, P200, P240 appeared at around 140°C, 180°C, 200°C, respectively. Either a single peak with a shoulder or double peaks were seen in the TSC of the corona poled P150. The lower peak or shoulder appeared around 180–190°C while the higher one appeared at a temperature slightly lower than the depolarization peak of the conventionally poled P240. These TSC peaks correspond to the glass transition temperature of the polymer, and the T_g of the corona poled P150 measured by DSC is shown in Table 1. The area poled by corona appeared to have lower T_g than the area where the corona was blocked during poling. This implies that the corona field might hinder the imidization of the amic acid since the rotational freedom of the molecule was decreased by the dipole alignment in the presence of the electric field. The broader depolarization peak of the P150 is attributable to a broader range of the T_g of the polymer as a result of the hindered imidization.

The value of remanent polarization (P_r) is obtained by integrating the depolarization current with respect to time. The partially cured, corona poled polyimides exhibited higher P_r values than the fully cured, conventionally poled ones. It appeared that P_r was higher for polyimides cured with lower final cure temperatures, as seen in Table 1. The highest value of P_r , about 38 mC/m² was achieved when the partially cured P150 was poled and imidized *in situ* under the corona discharge. The P150 partially-cured, corona poled polyimide exhibited three times higher P_r than the fully-cured, conventionally poled one. The P_r of the corona poled polyimides, however, was not uniform, with values ranging from 10 to 50 mC/m², possibly because of nonuniform field generation by the single corona tip used for the poling. The highest P_r value was obtained near the area below the tip, where more noticeable surface damage was observed.

The remanent polarization, P_r can be also estimated according to Equation (1). Assuming the poling field was 100 MV/m with the extrapolated value of $\Delta\epsilon$ at 1Hz, the values of P_r are calculated to be 19.8 and 13.4 mC/m² for the partially cured P150 and fully cured P240, respectively. The value for the P150, however, is in poor agreement with that measured experimentally (38 mC/m², corona poled). The agreement for the P240 (14 mC/m² conventionally poled at 80 MV/m) is much better. This is possibly due to underestimation of the applied field for the corona poling of the P150 and $\Delta\epsilon$ for actual poling (DC). For the corona poling, much higher poling fields can be applied without causing a catastrophic dielectric breakdown of the film since the arcing can be localized and does not propagate transversely if the film has a high resistivity.

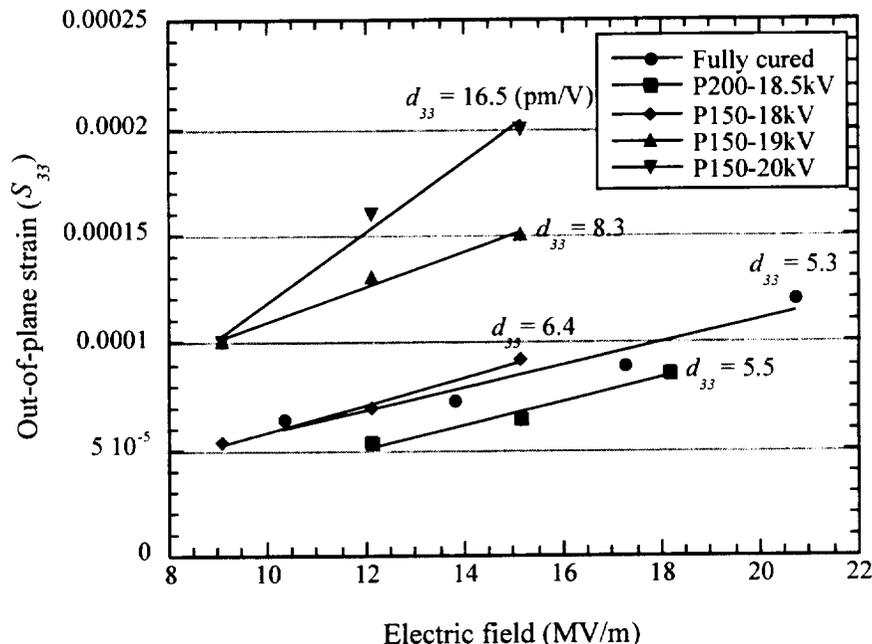


FIGURE 10. Out-of-plane strain as a function of the applied electric field: The piezoelectric strain coefficients (d_{33}) are shown as the slopes.

3.5. Piezoelectric strain coefficient. The piezoelectric strain coefficients (d_{33}) of the poled samples were calculated using Equation (4). This thickness strain (out-of-plane) was measured in response to the applied electric field. The strain (S_{33}) increased linearly with the applied electric field for all the specimens regardless of the cure and poling cycles. This linear relationship confirms the piezoelectric nature of the amorphous polyimide response. It is obvious that P150 exhibits higher displacement characteristics, and hence, higher strains than the P200. Figure 10 shows the piezoelectric strain coefficient (d_{33}) as a function of driving field. The conventionally poled P240 exhibited d_{33} of 5.3 pm/V and a similar value of 5.5 pm/V was obtained for the corona poled (at 18.5 kV) P200. The corona poled P150 showed a higher d_{33} than the conventionally poled P240, and the piezoelectric coefficient increased with the poling field. When poled at 20kV, the d_{33} of the corona poled P150 was 16.5 pm/V, which is three times higher than that of the conventionally poled P240. This value is about 43% of the value of PVDF, 38 pm/V, which was prepared and measured by the same procedure for comparison. The piezoelectricity of PVDF, however, begins to decrease rapidly above 70°C, while that of the P150 retains more than 90% of the initial value at room temperature after heating up to 150°C [11]. The thermal piezoelectric stability of this amorphous polyimide is potentially beneficial for use in micro-electro-mechanical systems (MEMS) devices and high temperature aerospace applications.

4. Conclusions. *In situ* poling and imidization of partially cured (β -CN)APB/ODPA was studied in an attempt to maximize the degree of dipolar orientation and the resultant piezoelectricity. Monomer dipole moments in (β -CN)APB/ODPA were studied using computational chemistry, which predicted that the dipole moment of a partially cured oriented amic acid (open imide ring) is four times higher than the fully imidized oriented closed ring. The partially cured, corona poled polymers exhibited higher dielectric relaxation strength ($\Delta\epsilon$), remanent polarization (P_r) and piezoelectric strain coefficient (d_{33}) than the fully cured, conventionally poled one, in agreement with the computational analysis. The piezoelectric strain coefficient of a polyimide prepared by the present method can be further increased by adding higher

dipole concentration into the monomer unit. Therefore, this thermally stable polyimide may be an attractive alternative to PVDF for high temperature piezoelectric applications.

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